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REVERSIBLE POLYMER HYDROGELS

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ABSTRACT

Temperature sensitive hydrogels based on N-isopropyl acrylamide (NIPA) and acryloyl glucosamine (AG) were synthesized using ammonium persulfate (APS) as initiator, N,N,N',N'-tetramethylenediamine (TEMED) as activator, and N,N'-methylene bisacrylamide (BIS) as cross-linker. The hydrogels were characterized using FTIR spectral analysis to investigate the chemical composition of the hydrogels. Swelling studies of the gel in water at room temperature to relate the swelling characteristics to the chemical composition were conducted. Further, the critical swelling temperature of the gels was determined on the basis of absorbance of radiation by the gels. The gels were used in separating the water contaminants such as As^{+3,+5}, Cr^{+3,+6}, RDX and HMX from aqueous medium. The results of the preliminary study demonstrated that the gels are highly stable and capable of removing pollutants from water.

1. INTRODUCTION

Hydrogels are complex networks of cross-linked polymers capable of retaining large amounts of water. Certain gels respond to minute changes in their environment such as temperature, pH, and ionic composition. For example, some acrylic based gels can absorb water at 25°C and desorb at 35°C. Hydrogel swelling occurs when a dry or partially swollen gel is placed in a solvent, causing the cross-linked network to expand (Bomberg and Ron 1998). This reaction is thermodynamically driven; the swelling force that causes the network to expand is counterbalanced by elastic and hydrophobic repulsive forces within the polymer gel. The hydrogels can be reused several times without appreciable loss of absorption capacity. Potential biomedical (drug delivery systems, enzyme encapsulation), food protein separation, and analytical applications are extensively researched. However, there has been little activity for developing environmental applications. By adjusting the gel environment, cost effective sorption and separation processes can be designed.

The primary objective of this research is to synthesize and characterize several environmentally responsive polymer hydrogels and define their sorption and separation properties for explosives (RDX and HMX) and other emerg-

ing energetic compounds, and Army related metals (e.g. Cr^{+3,+6} and As^{+3,+5}). This presentation, however, focuses on synthesis and characterization of one system of hydrogels by copolymerization of poly (N-isopropylacrylamide) (NIPA), and acryloyl glucosamine (AG) a derivative of chitosan, a biopolymer from shellfish. This research would help the Army to proactively prepare for dealing with the environmental consequences of the munitions compounds, with reversible gels to selectively absorb environmental contaminants. In addition these gels may find niche applications in biosensor development, bacterial immobilization, enzyme encapsulation, and in polymer-network-pumps in microfluidic devices.

2. EXPERIMENTAL

2.1 Approach

The experimental approach involved: (1) synthesis of hydrogels using solution polymerization, (2) swell tests on gels to determine swelling ratio, (3) Fourier Transform Infrared Spectroscopy (FTIR) to elucidate chemical structure, and Scanning Electron Microscopy (SEM) to observe surface morphology on gels, and (4) determination of critical temperatures for the gels.

2.2 Synthesis of hydrogels

Four NIPA-AG gels of varying compositions were synthesized. Ammonium persulfate (APS), and N, N, N', N'-tetramethylenediamine (TEMED) were used as activators for co-polymerization, and N,N'-methylene bisacrylamide (BIS) as a cross-linker. The synthesis involved a detailed solution polymerization protocol (Boddu, et al., 2008).

2.3 Materials

N-isopropylacrylamide (97%), D-(+)-Glucosamine hydrochloride (99%), triethylamine (99.5%), acryloyl chloride (98%), N,N,N',N'-tetramethylenediamine (98%) and ammonium persulfate (98+%) were procured from Sigma Aldrich-USA. N,N'-methylene bisacrylamide (99.5%), used as a cross-linker, was purchased from Fluka BioChemical-USA. Deionized (DI) water was generated using US-Filter deionizer (18M Ω -grade). N,N,N',N'-tetramethylenediamine (TEMED), ammonium persulfate (APS), and N,N'-

methylene bisacrylamide (BIS) were used as activator, initiator, and cross-linker, respectively.

2.4 Preparation of acryloyl glucosamine

Acryloyl Glucosamine (AGA) was prepared following the procedure described by Yu et al. (2008). 5.0 g of D-(+)-glucosamine hydrochloride was dissolved in 100 mL of de-ionized water and placed in an ice bath at $>5^{\circ}\text{C}$ and purged with N_2 gas for 20 minutes; 3.25 mL of triethylamine and 1.885 mL of acryloyl chloride were added drop wise while stirring the contents. After the addition of the entire acryloyl chloride, the reaction continued with stirring for 4 h between $0\text{--}5^{\circ}\text{C}$ and 20 h at room temperature. Then triethylamine hydrochloride salts were removed by filtration. AGA formed was recrystallized twice in ethanol/ethyl acetate mixture.

2.5 Preparation of NIPA-co-AGA hydrogels

The amounts of starting materials used in the synthesis of NIPA-co-AGA hydrogels are listed in Table 1. To synthesize the gels, the starting materials such as NIPA, AGA, and BIS solutions were added to deionized water. The resulting solution was stirred in an ice bath under N_2 for 20 minutes. APS solution and TEMED were added and the mixture was placed in a Teflon frame between two glass plates to polymerize. The gels were allowed to polymerize for two days at room temperature. The gels were cleaned by immersion in water which was changed four times. After the gels were leached, they were placed on a plastic filter and kept in an oven for a day to totally remove all the water. The gels were then stored in a refrigerator for subsequent characterization and evaluation of its potential in removing contaminants from water. A schematic representation of the formation of NIPA-co-AGA hydrogel is shown in Fig.1.

Table 1. Poly (N-isopropylacrylamide) -Acryloyl Glucosamine Gel Compositions

| Gel ID | NIPA, mol% | AG, mol% | BIS, mM | Q, $\frac{\text{g H}_2\text{O}}{\text{g dry gel}}$ | Critical Solution Temp. $^{\circ}\text{C}$ |
|--------|------------|----------|---------|--|--|
| 6-3-1 | 65.93 | 34.07 | 0.33 | 293.2 | 50.3 -56.3 |
| 6-3-2 | 82.81 | 17.19 | 0.38 | 124.1 | 42.5 – 51.2 |
| 6-3-3 | 90.50 | 9.50 | 0.41 | 101.8 | 33.1 – 42.1 |
| 6-3-4 | 93.87 | 6.13 | 0.42 | 75.6 | 30.9 – 38.9 |

2.6 Characterization

SEMs and FTIR spectra were obtained for all the four gel compositions. Swelling characterizations were carried out in 15 mL vials. The vials were filled with deionized water. The vials were left at room temperature on a shaker table for 3~4 days for equilibration. The excess water was then drained and the amount of water absorbed per gram of dry gel was calculated.

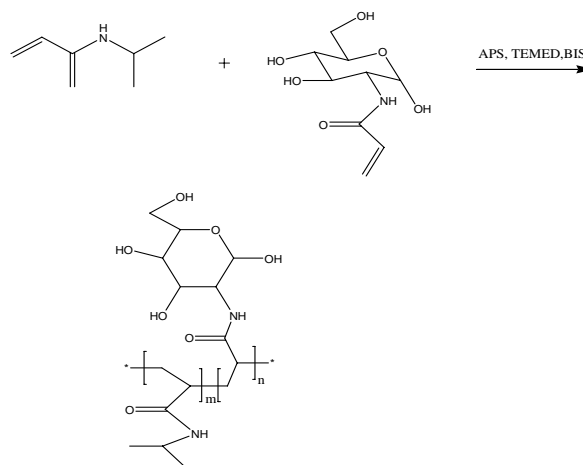


Fig. 1. Formation of NIPA-co-AGA hydrogel.

Critical temperatures were determined by UV/V spectroscopy. Swollen gels were placed in temperature controlled glass cuvettes. The temperature was gradually increased and spectra were repeatedly obtained. The swollen gels are transparent but the collapsed gels are opaque, so absorbance values rise sharply when the gels collapse. Critical temperatures were obtained by plotting absorbance against temperature.

3. RESULTS

The composition, the equilibrium water absorption capacity Q, and critical temperatures for each composition of the hydrogels are listed in Table 1. Typical SEM micrograph and FTIR spectrum are shown in Figures 2 and 3. Figures 4 (a) and (b) show collapsed gel and a swollen gel. Figure 5 shows the results of light absorption values as a function of temperature.

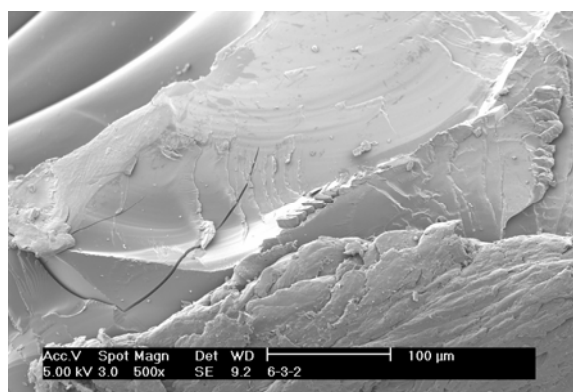
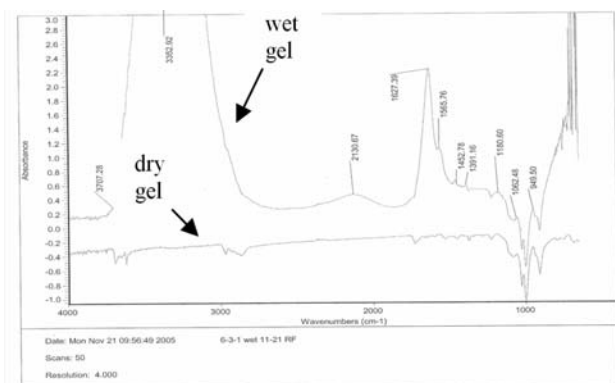


Fig. 2. SEM of Gel 6-3-2 at 500x Magnification.



absorb the larger amount of water. Critical temperatures are approximated from the graphs as a range. The temperature ranges are summarized in Table 1 and expected to be accurate to $\pm 1^\circ\text{C}$. The study of potential applications of these gels as absorbents or thick filters for molecular separations is in progress. The results of separation of RDX, HMX and other metal ions and cyclical swelling will be presented elsewhere.

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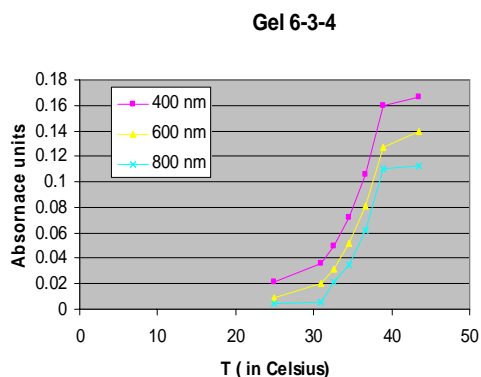
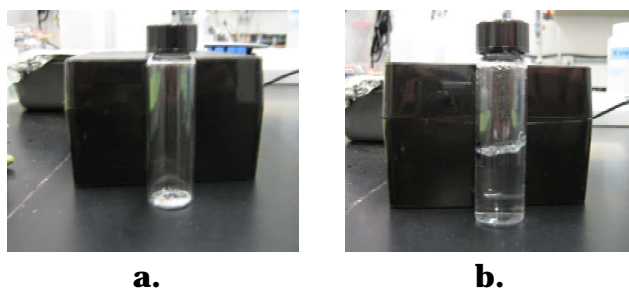


Fig. 5. Temperature vs. absorbance for gel 6-3-4.

4. DISCUSSION

The SEM micrographs (e.g., Figure 2) show the surface morphology and homogeneous nature of the gels. All the FTIR spectra (Figure 3) share three common peaks, around 1650, 2120, and 3330 cm^{-1} . The 1650 peak is most likely a C=O peak. The 2120 peak is possibly a triple bonded C-N bond. These bonds could be between glucosamine monomer and the cross-linker, N,N'-methylene bisacrylamide. The large, broad peak at about 3350 cm^{-1} , and other peaks at 2130, 1630, and 1565 cm^{-1} appear only when the gel has been swollen. Thus, these peaks are most likely attributed to a water molecule that has bonded to the polymer and dissociated from one of the protons, resulting in an OH peak. This confirms that the gels bond with water through more than one mechanism. It is observed that the gels with the highest component of acryloyl glucosamine were able to